Theory for the Change of the Bond Character in Divalent-Metal Clusters

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To determine the size dependence of the bonding in divalent-metal clusters we use a many-electron Hamiltonian describing the interplay between van der Waals (vdW) and covalent interactions. Using a saddle-point slave-boson method and taking into account the size-dependent screening of charge fluctuations, we obtain for Hg_n a sharp transition from vdW to covalent bonding for increasing n. We show also, by solving the model Hamiltonian exactly, that for divalent metals vdW and covalent bonding coexist already in the dimers.

Divalent-metal atoms are characterized by a closed-shell electronic configuration (ns^2np^0), whereas the corresponding solids have s and p bands which overlap and thus give rise to metallic bulk behavior. Therefore, clusters of these elements are expected to exhibit a strong change in their electronic properties as a function of cluster size. This physical picture seems to be confirmed by recent experiments for Hg_n [1–3], which are interpreted as reflecting a size-dependent transition from van der Waals (vdW) to covalent bonding and for larger clusters to metallic bonding [4]. So far, an electronic theory for the size dependence of the bonding and consequently for the transition from van der Waals–like to covalent to metalliclike bonding is lacking. It is the goal of this Letter to present such a theory treating vdW and covalent interactions on the same electronic level.

The dynamics of the valence electrons in divalent-metal clusters is dominated by two distinct interactions: The vdW interactions (induced dipole-dipole), which involve mainly *intra-atomic sp* excitations [see inset (b) of Fig. 1], and the covalent interactions, which result from *in-teratomic sp* transitions and consequently involve charge fluctuations and Coulomb repulsions [see inset (a) of Fig. 1]. Since the same electrons take part in both cohesion processes, there is an *interplay* between vdW and covalent interactions which must be taken carefully into account. Consequently, we propose the Hamiltonian [5]

$$H = H_{vdW} + H_{cov}. \tag{1}$$

Here vdW interactions involving *intra-atomic sp* excitations are described by

$$H_{vdW} = \frac{1}{2} \sum_{i \neq j, p\sigma\sigma'} V_{ij} c^\dagger_{ip\sigma} c_{is\sigma} c^\dagger_{jp\sigma'} c_{js\sigma'}$$
$$- \frac{1}{2} \sum_{i \neq j, p\sigma\sigma'} V_{ij} c^\dagger_{ip\sigma} c_{is\sigma} c^\dagger_{js\sigma'} c_{jp\sigma'} + \text{H.c.}, \tag{2}$$

and covalent interactions due to *interatomic* transitions involving s and p states are described by

$$H_{cov} = \sum_{i\beta\sigma} \varepsilon_\beta c^\dagger_{i\beta\sigma} c_{i\beta\sigma} + \sum_{i \neq j, \beta\gamma} t^{ij}_{\beta\gamma} c^\dagger_{i\beta\sigma} c_{j\gamma\sigma}$$
$$+ \sum_{i, \beta\sigma \neq \gamma\sigma'} U_{\beta\gamma} n_{i\beta\sigma} n_{i\gamma\sigma'}. \tag{3}$$

The operators $c^\dagger_{i\beta\sigma}$, $c_{i\beta\sigma}$, and $n_{i\beta\sigma} = c^\dagger_{i\beta\sigma} c_{i\beta\sigma}$ refer to the creation, annihilation, and occupation-number operators for an electron with spin σ at site i and orbital $\beta = s,p$. V_{ij} is the vdW coupling constant between sites i and j, which depends on the sp atomic energy gap Δ, the sp contribution to the atomic polarizability α, and the inter-atomic distance r_{ij} ($V_{ij} \propto \Delta\alpha/r^3_{ij}$) [6]. H_{cov} is a two-band Hubbard Hamiltonian, where ε_β refer to the on-site energies, $t^{ij}_{\beta\gamma}$ to the hopping integrals, and $U_{\beta\gamma}$ to the on-site Coulomb interactions. The Coulomb energy U involved in a local charge fluctuation [e.g., $U = 2U_{sp} - U_{ss}$ from the inset (a) of Fig. 1] actually depends on the cluster size due to the size dependence of screening. For small clusters we expect U to be a sensitive function of the coordination number, as will be discussed below.

An exact solution of the many-body Hamiltonian H is not available at present. A correct treatment of the interplay between vdW and covalent bonding inherent in H requires one to take into account explicitly the different local electronic configurations which contribute to the correlated ground-state wave function. Therefore, we in-
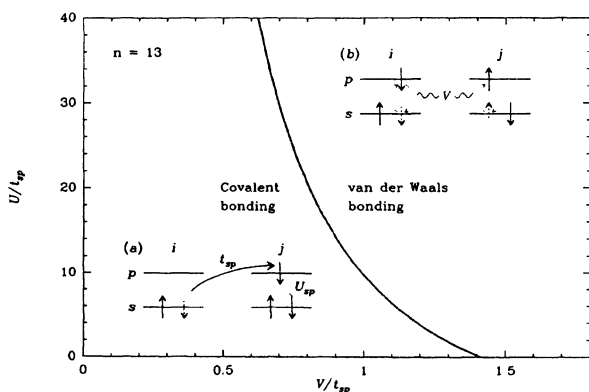

FIG. 1. Phase diagram for vdW and covalent bonding as a function of the Coulomb energy of a charge fluctuation U and the vdW coupling constant V (both scaled by t_{sp}) for $n = 13$ atoms (see Refs. [13] and [14]). In the inset figures the dominant electronic excitations responsible for (a) covalent and (b) vdW interactions are illustrated.

troduce, in analogy with the slave-boson method of Ref. [7], a set of boson operators which project onto the atomic configurations illustrated in the insets of Fig. 1. The creation (annihilation) operators $s_{i\sigma}^\dagger$ $(s_{i\sigma})$, $d_i^\dagger$ (d_i), $m_{i\sigma\bar\sigma}^\dagger$ $(m_{i\sigma\bar\sigma})$, and $p_{i\sigma}^\dagger$ $(p_{i\sigma})$ correspond, respectively, to the configurations ns^1, ns^2, ns^1np^1 (with opposite spins), and ns^2np^1. The physical states in the enlarged Hilbert space (including fermions and bosons) must satisfy

$$n_{s\sigma} = s_{i\sigma}^\dagger s_{i\sigma} + d_i^\dagger d_i + m_{i\sigma\bar\sigma}^\dagger m_{i\sigma\bar\sigma} + \sum_{\sigma'} p_{i\sigma'}^\dagger p_{i\sigma'}, \qquad n_{p\sigma} = p_{i\sigma}^\dagger p_{i\sigma} + m_{i\bar\sigma\sigma}^\dagger m_{i\bar\sigma\sigma}, \tag{4}$$

and the normalization condition

$$d_i^\dagger d_i + \sum_\sigma (s_{i\sigma}^\dagger s_{i\sigma} + p_{i\sigma}^\dagger p_{i\sigma} + m_{i\sigma\bar\sigma}^\dagger m_{i\sigma\bar\sigma}) = 1. \tag{5}$$

Notice that atomic configurations having no s or more than one p electron have been projected out, since they are not expected to be relevant for the ground state of small neutral Hg_n clusters.

In the new representation the Hamiltonian is given in terms of the fermion and boson operators as

$$\tilde H = \sum_{i\beta\sigma} \varepsilon_\beta c_{i\beta\sigma}^\dagger c_{i\beta\sigma} + \tfrac{1}{2} \sum_{i\neq j,\sigma\sigma'} V_{ij}\Omega_{i\sigma}^\dagger \Omega_{j\sigma'}^\dagger c_{ip\sigma'}^\dagger c_{is\sigma} c_{jp\sigma'}^\dagger c_{js\sigma'} - \tfrac{1}{2} \sum_{i\neq j,\sigma\sigma'} V_{ij}\Omega_{i\sigma}^\dagger \Omega_{j\sigma'} c_{ip\sigma'}^\dagger c_{is\sigma} c_{js\sigma'}^\dagger c_{jp\sigma'} + \mathrm{H.c.}$$

$$+ \sum_{i\neq j,\beta\gamma\sigma} t_{\beta\gamma}^{ij} Z_{i\beta\sigma}^\dagger Z_{j\gamma\sigma} c_{i\beta\sigma}^\dagger c_{j\gamma\sigma} + U_{ss}\sum_i d_i^\dagger d_i + (U_{ss}+2U_{sp})\sum_{i\sigma} p_{i\sigma}^\dagger p_{i\sigma} + U_{sp}\sum_{i\sigma} m_{i\sigma\bar\sigma}^\dagger m_{i\sigma\bar\sigma}. \tag{6}$$

The operator $\Omega_{i\sigma}^\dagger$ $(\Omega_{i\sigma})$ changes the boson occupations if an intra-atomic sp excitation is created (annihilated) at site i. $\Omega_{i\sigma}^\dagger$ is given by

$$\Omega_{i\sigma}^\dagger = (1 - s_{i\sigma}^\dagger s_{i\sigma} - d_i^\dagger d_i - m_{i\sigma\bar\sigma}^\dagger m_{i\sigma\bar\sigma} - p_{i\bar\sigma}^\dagger p_{i\bar\sigma})^{-1/2}$$

$$\times m_{i\bar\sigma\sigma}^\dagger d_i (1 - m_{i\bar\sigma\sigma}^\dagger m_{i\bar\sigma\sigma})^{-1/2}. \tag{7}$$

Similarly, $Z_{i\beta\sigma}^\dagger$ $(Z_{i\beta\sigma})$ changes the boson occupations according to the creation (annihilation) of an electron of spin σ at site i and orbital β. $Z_{i\beta\sigma}$ is the natural generalization for two bands of the operator $\tilde z_{i\sigma}$ of Ref. [7] [5,8].

The ground-state properties are evaluated in the saddle-point approximation (SPA) [7]. Here, the boson operators $p_{i\sigma}^\dagger$, $d_i^\dagger$, etc., are taken as numbers determined by minimizing the ground-state energy [taking into account the constraints (4) and (5)]. Thus, both the hopping elements and the vdW coupling constant become renormalized by the factors

$$q_{\beta\gamma\sigma}^t = \langle Z_{\beta\sigma}^\dagger Z_{\gamma\sigma}\rangle = p^2(d+m)^2/(m^2+p^2)(m^2+3p^2+d^2)$$

and

$$q_{\sigma\sigma'}^V = \langle \Omega_\sigma^\dagger \Omega_{\sigma'}^\dagger\rangle = d^2 m^2/(m^2+2p^2)(m^2+4p^2+d^2),$$

respectively [9]. This reflects in a physically transparent way the interplay between covalent and vdW bonding. The factors q^t and q^V can be interpreted as order parameters. For example, $q^t = 0$ means that triple and single occupations vanish, implying localized electrons (vdW bonding), whereas $q^t = 1$ means maximal covalent bonding (delocalized electrons). A transition from localized to delocalized electronic states should be reflected in the cluster-size dependence of q^t and q^V. The competition between itinerancy and vdW interactions can be already seen by noting that $0 \leq q^t + q^V \leq 1$.

Using Eqs. (4)–(6) in the SPA the ground-state energy

E_n of a cluster can be written as

$$E_n = 2\sum_\beta \int d\varepsilon (\varepsilon - \tilde\varepsilon_\beta)\tilde N_\beta(\varepsilon) + \sum_{ij} \frac{(q^V V_{ij})^2}{\tilde\varepsilon_s - \tilde\varepsilon_p} + 2nUp^2$$

$$+ 2n\lambda_s^{(2)}(d^2+3p^2+m^2) + 2n\lambda_p^{(2)}(p^2+m^2)$$

$$+ n\lambda^{(1)}(d^2+4p^2+2m^2), \tag{8}$$

where $\tilde\varepsilon_\beta = \varepsilon_\beta + \lambda_\beta^{(2)}$, and $\lambda_\beta^{(2)},\lambda^{(1)}$ are the Lagrange multipliers resulting from the constraints (4) and (5). The first term in Eq. (8) is the kinetic energy, where $\tilde N_s$ ($\tilde N_p$) refers to the total s (p) density of states calculated using the renormalized hopping elements $\tilde t_{\beta\gamma}^{ij} = q^t t_{\beta\gamma}^{ij}$ and the shifted on-site energies $\tilde\varepsilon_\beta$. The second term refers to the vdW energy, which is calculated to second order in $\tilde V = q^V V$. This is a good approximation, since $\tilde\varepsilon_p - \tilde\varepsilon_s \gg \tilde V$. The third term is the Coulomb energy due to interatomic charge fluctuations [see inset (a) of Fig. 1]. For simplicity we assume $U_{\beta\gamma} = U$ and we drop the site dependences (i.e., $t_{\beta\gamma}^{ij} = t_{\beta\gamma}$ and $V_{ij} = V$) by restricting the sums to nearest neighbors. The saddle-point (SP) values of the boson fields and renormalization factors q^t and q^V have been obtained by minimizing $E_n(s^2,m^2,p^2,d^2)$ for clusters with $n \leq 43$ atoms and different values of the interaction parameters U and V [10].

For $V = 0$ we obtain, for all cluster sizes, a single minimum in E_n having $q^t = 1$ and $q^V = 0$. This corresponds to the SP solution of the two-band Hubbard model with two electrons per site. Here, $p^2 = s^2 \neq 0$ [$p^2 \sim t_{sp}^2/(\Delta+U)^2$ for $U \to \infty$], whereas m^2 is negligible ($p^2 \gg m^2$). The binding energy $E_n(q^t = 1)$ decreases for increasing U, and particularly $E_n \sim t_{sp}^2/(\Delta+U) \to 0$ for $U \to \infty$. The binding is, as expected, exclusively due to interatomic charge fluctuations.

New features appear if vdW interactions are included. For $V \neq 0$, in addition to the covalent minimum a second

SP is found in E_n having $q^V = 1$ and $m^2 \sim (V/\Delta)^2 \neq 0$, while $q' = 0$ and $p^2 \ll m^2$. At this SP the excitations illustrated in the inset (b) of Fig. 1 dominate and the energy is independent of U ($E_n \sim V^2/\Delta$). The bonding is of pure vdW character. The SP which is actually relevant for the cluster ground state is the one with the lowest energy. The resulting phase diagram for the bond character as a function of U and V is shown in Fig. 1 for a cluster with $n = 13$ atoms [11]. A similar phase diagram is obtained for other cluster sizes ($n \leq 43$) provided that the s and p bands do not overlap. The importance of treating vdW and covalent interactions on the same microscopic level is evident. Furthermore, from Fig. 1 one may conclude already quite generally that a transition from vdW to covalent bonding can occur for increasing n, since the energy U involved in a local charge fluctuation should decrease with increasing n due to screening.

To demonstrate that our theory is able to explain quantitatively the change in the bond character of Hg_n clusters as a function of cluster size, we estimate the interaction parameters V and U as follows. The vdW coupling constant [5] $V = c\alpha\Delta/r_0^3 = 0.55$ eV is obtained from the atomic polarizability per valence electron $\alpha = 2.85$ Å^3, the average between the dimer and the bulk nearest-neighbor distances $r_0 = 3.33$ Å, and the constant $c \simeq 1.25$, which was determined by fitting to the binding energy of rare-gas dimers. The Coulomb energy U involved in an interatomic charge fluctuation is given by $U = U_0 - U_1 - \Delta U$, where $U_0 = 2U_{sp} - U_{ss}$ stands for the increase of the intra-atomic Coulomb repulsion, and $U_1 \simeq (U_0^{-1} + r_0/e^2)^{-1}$ for the remaining electron-hole interaction [see inset (a) of Fig. 1]. ΔU takes into account the screening of interatomic charge fluctuations due to the polarization of the atoms surrounding the electron-hole pair. Using

second-order perturbation theory one obtains for the screening resulting from the charge-dipole interaction

$$\Delta U = \frac{\alpha e^2}{r_0^4} \left\langle \sum_k{}' \left[\left(\frac{r_0}{r_{ki}}\right)^4 + \left(\frac{r_0}{r_{kj}}\right)^4 - 2r_0^4 \frac{\mathbf{r}_{ki} \cdot \mathbf{r}_{kj}}{r_{ki}^3 r_{kj}^3} + 1 \right] \right\rangle_{ij},$$
$$(9)$$

where $\langle \cdots \rangle_{ij}$ indicates cluster average through all nearest neighbors ij at which the charge fluctuation occurs. As physically expected, ΔU yields a reduction of U with increasing n due to the increase of the coordination number [12].

In Fig. 2 results are given for the bond character of Hg_n clusters as a function of U_0 and n [11]. The phase boundary is determined using Eqs. (8) and (9) as the value of U_0 for which n is equal to the critical cluster size n_c at which the transition from vdW to covalent bonding occurs. An approximated realistic value of U_0 for Hg is indicated [13]. According to this the transition occurs in Hg_n at $n_c \simeq 10$–20 atoms. Although the results depend implicitly on the other parameters (V, Δ, t_{sp}), Fig. 2 can be interpreted as a phase diagram for the bond character. Notice that the existence of a transition is restricted to a certain range of values for U_0. For instance, if $U_0 < 5$ eV, the system would be covalent already for $n = 2$. For $U_0 > 9$ eV vdW behavior results for all cluster sizes, as we obtain for rare-gas clusters. If ΔU is neglected the range for the occurrence of the transition is reduced. In the inset of Fig. 2 the size dependence of the hopping renormalization factor Q^t of Hg_n is shown. For $n \leq 13$, $q' = 0$ implies that the electrons are localized. Only vdW bonding is present ($q^V = 1$) and the binding energy per bond is roughly independent of n. At $n \simeq 13$ there is a crossing of the SP solutions and the character of the
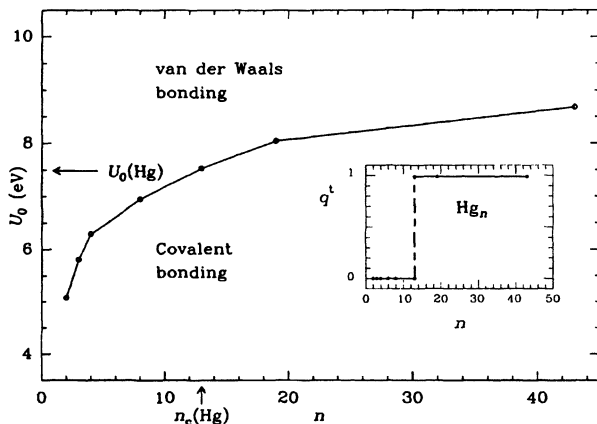

FIG. 2. Phase diagram for vdW and covalent bonding as a function of the intra-atomic Coulomb repulsion U_0 and n. Estimating $U_0(Hg) = 7.5$ eV, one obtains $n_c(Hg) \simeq 13$ atoms. Inset: The resulting behavior of q' for Hg_n.
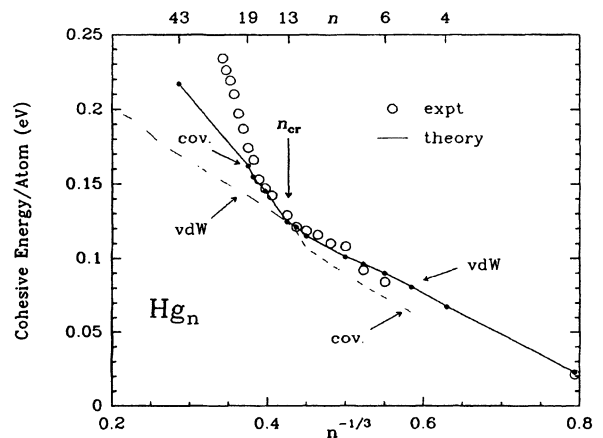

FIG. 3. Size dependence of the cohesive energy per atom. Open circles refer to the experimental values (Ref. [3]), and solid circles to the theory (this work). The dashed lines indicate results for the unstable covalent state ($n < 13$) and the unstable vdW state ($n > 13$).

bonding changes. For $n > 13$, we obtain $q' = 1$ which physically means that the valence electrons delocalize to form covalent bonds, or for larger clusters metallic bonds, and vdW bonding is suppressed ($q^V = 0$). Now the binding energy per bond increases with n. This change in the bond character is also reflected in the size dependence of the cohesive energy $E_{coh}(n)$ [14]. As shown in Fig. 3, a change of the slope occurs at $n \simeq 13$, which results from the crossing of the vdW and covalent SP. Quantitatively our results are in good agreement with experiment [3]. The discrepancies for $n > 19$ are probably due to the approximation used for the screening [Eq. (9)], which might tend to overestimate the repulsive Coulomb energy of charge fluctuations in clusters with dominant covalent character. The calculated suppression of band formation ($q' = 0$) for $n < n_c$ and the change to delocalized valence electrons ($q' = 1$) for $n > n_c$ is also in agreement with the following observations on Hg$_n$: For $n \lesssim 13$ the $5d \rightarrow 6p$ autoionization lines are symmetric (atomiclike) and the line widths are approximately independent of n, while for $n \gtrsim 20$ they broaden asymmetrically indicating $6p$ band formation [1]. For $n \lesssim 13$ the size dependence of the ionization energy I_n is very similar to that of vdW clusters, while for $n \gtrsim 13$ I_n decreases more rapidly indicating $6s$ band broadening [2].

In order to study the interplay between vdW and covalent bonding beyond the SPA we diagonalize exactly the Hamiltonian H [Eqs. (1)–(3)] for $n = 2$. For $V \neq 0$, $t_{\beta\gamma} \neq 0$, and finite U, we obtain coexistence of vdW and covalent bonding. For instance, we estimate that the vdW contribution to the cohesive energy is more dominant for Hg$_2$ and Mg$_2$ ($\sim 80\%$) than for Ca$_2$ ($\sim 60\%$) [5]. The origin of the coexistence can be understood by noting that the electronic configurations involved in vdW and covalent bonding are interconnected by the terms $t_{sp}c_{ip\sigma}^\dagger c_{js\sigma}$ in H, for example.

Thus, quantum fluctuations between the vdW and covalent SP are present, which cause the actual ground state to be a combination of both vdW and covalent contributions.

Consequently, the transition from vdW to covalent bonding as a function of cluster size should be somewhat smoother than what the SPA calculations yield (Fig. 2).

The exact results ($n = 2$) agree with the SP slave-boson calculations. For instance, the boundary between vdW and covalent behavior as a function of V/t_{sp} and U/t_{sp} compares well with the SPA results given in Fig. 1. The physical picture supplied by the slave-boson calculations seems to account for the essential features of the character of the bonding in divalent-metal clusters.

Summarizing, we have calculated, for the first time,

the transition from vdW to covalent bonding in Hg$_n$ clusters. The importance of treating vdW and covalent interactions on the same electronic level has been demonstrated. Our theory should serve as a basis for calculating other electronic properties of divalent-metal clusters.

[1] C. Bréchignac, M. Broyer, Ph. Cahuzac, G. Delacretaz, P. Labastie, J. P. Wolf, and L. Wöste, Phys. Rev. Lett. **60**, 275 (1988).

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[5] Further details will be published elsewhere.

[6] In fact, the coupling constants for the first and second terms in H_{vdW} should be different due to Coulomb interactions. However, this has no consequences for the ground-state properties discussed here.

[7] G. Kotliar and A. E. Ruckenstein, Phys. Rev. Lett. **57**, 1362 (1986).

[8] In the SPA, $Z_{i\sigma}$ and $\Omega_{i\sigma}$ yield for all band fillings the exact result both for the noninteracting limit ($U = 0$, $V = 0$) and the pure vdW limit ($t = 0$). See also Ref. [7].

[9] For simplicity, the site-dependent boson fields have been replaced by their respective cluster averages s^2, d^2, etc.

[10] Results shown in Figs. 1–3 were obtained by using the close-packed structures given in Ref. [4] (i.e., for $n \geq 13$ fcc-like). Our results and conclusions were checked to be insensitive to the details of the cluster structure.

[11] We use $\Delta = 5.8$ eV, $t_{sp} = 0.5$ eV, $t_{ss} = 0.44$ eV, and $t_{pp} = 0.73$ eV, which correspond approximately to Hg (Ref. [4]).

[12] A more accurate treatment of the size-dependent screening is, of course, desirable. However, such improvements would not change our conclusions.

[13] C. Moore, *Atomic Energy Levels*, National Bureau of Standards Circular No. 467 (U.S. GPO, Washington, DC, 1958).

[14] $E_{coh}(n) = -[E_n + (z/2)E_{BM}]/n$. Here z is the average coordination number and E_{BM} is a constant core-core repulsive energy, which was fitted to the experimental $E_{coh}(2)$ and has no influence on the *change* of the slope in Fig. 3.